Economy Perspective of Biofuel - A Comprehensive Review

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ABSTRACT:
The term biofuel is referred to liquid, gas and solid fuels predominantly produced from biomass. Biofuels include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. Biofuels include bioethanol, biomethanol, vegetable oils, biodiesel, biogas, bio-synthetic gas (bio-syngas), bio-oil, bio-char, Fischer-Tropsch liquids, and biohydrogen. Most traditional biofuels, such as ethanol from corn, wheat, or sugar beets, and biodiesel from oil seeds, are produced from classic agricultural food crops that require high-quality agricultural land for growth. Due to its environmental merits, the share of biofuel in the automotive fuel market will grow fast in the next decade. There are several reasons for biofuels to be considered as relevant technologies by both developing and industrialized countries. Biofuels include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. Sustainable economic and industrial growth requires safe, sustainable resources of energy. For the future re-arrangement of a sustainable economy to biological raw materials, completely new approaches in research and development, production, and economy are necessary. The 'first-generation' biofuels appear unsustainable because of the potential stress that their production places on food commodities. For organic chemicals and materials these needs to follow a biorefinery model under environmentally sustainable conditions. Where these operate at present, their product range is largely limited to simple materials (i.e. cellulose, ethanol, and biofuels). Second generation biorefineries need to build on the need for sustainable chemical products through modern and proven green chemical technologies such as bioprocessing including pyrolysis, Fisher Tropsch, and other catalytic processes in order to make more complex molecules and materials on which a future sustainable society will be based. This review focuses on cost effective technologies and the processes to convert biomass into useful liquid biofuels and bioproducts.

Key words: First generation biofuel, Second generation biofuel, Biorefinery, Policy, Renewable energy

INTRODUCTION

The increasing industrialization and motorization of the world has led to a steep rise for the demand of petroleum-based fuels [1]. Today fossil fuels take up 80% of the primary energy consumed in the world, of which 58% alone is consumed by the transport sector [2]. The sources of these fossil fuels are becoming exhausted and found major contribution in greenhouse gas (GHG) emissions by consumption of fossil fuels to fulfil the energy demand [3,5], which leads to many negative effects including climate change, receding of glaciers, rise in sea level, loss of biodiversity, etc. [6]. Increasing energy demand leads to an increase in crude oil price, directly affected to global economic activity [7]. Progressive depletion of conventional fossil fuels with increasing energy consumption and GHG emissions have led to a move towards alternative, renewable, sustainable, efficient and cost-effective energy sources with lesser emissions [4,5,8,9].Biofuels are referred to liquid, gas and solid fuels predominantly produced from biomass. A variety of fuels can be produced from biomass such as ethanol, methanol, biodiesel, Fischer-Tropsch diesel, hydrogen and methane [12]. Biofuels have emerged as one of the most strategically important sustainable fuel sources and are considered an important way of progress for limiting greenhouse gas emissions, improving air quality and finding new energetic resources [13].

Renewable and carbon neutral biofuels are necessary for environmental and economic sustainability. People will always need fuel for living and heating, and since the demand for oil has increased, production from large oil fields is declining at the rate of 4.5% annually, subsequently the world production of oil is expected to peak in coming years. A worrying statistic is that global production of oil and gas is approaching its maximum and the world is now finding one new barrel of oil for every four it consumes [14]. Hence, as an alternative to fossil fuels, biofuels have been portrayed as

a future leading supplier of energy sources that have the ability to increase the security of supply, reduce the vehicle emissions and provide a steady income for farmers.

Biofuels are important because they replace petroleum fuels. An increasing number of developed and developing countries found biofuels as a key to reducing reliance on foreign oil, lowering GHG emissions and meeting rural development goals [15-17]. Between1980 and 2005, worldwide production of biofuels increased by an order of magnitude from 4.4 to 50.1 billion litres [16, 18], with further dramatic increases in future [19]. Biofuels are considered to be most promising in the short-term as their market maturity is above those of the other options [20].

FIRST GENERATION BIOFUELS

The dramatic rise in oil prices seen in the last decade has also enabled liquid biofuels to become cost-competitive with petroleum- based transportation fuels, and this has led to a surge in research and production around the world. The three main types of first generation biofuels used commercially are biodiesel (bio-esters), ethanol, and biogas of which worldwide large quantities have been produced so far and for which the production process is considered 'established technology'. Biodiesel is a substitute of diesel and is produced through transesterification of vegetable oils, and residual oils and fats, with minor engine modifications; it can serve as a full substitute as well. Bioethanol is a substitute of gasoline and it is a full substitute for gasoline in so-called flexi-fuel vehicles. It is derived from sugar or starch through fermentation.

Bioethanol can also serve as feedstock for ethyl tertiary butyl ether (ETBE) which blends more easily with gasoline. Biogas, or biomethane, is a fuel that can be used in gasoline vehicles with slight adaptations. It can be produced through

anaerobic digestion of liquid manure and other digestible feedstock. At present, biodiesel, bioethanol and biogas are produced from commodities that are also used for food. The demands of edibles oils are increasing trend, so it difficult to use the agricultural food crop for biofuel production [22]. There are some potential crops for biodiesel production, which can be taken up as Industrial crop on unproductive lands. Such multipurpose uses oilseeds crops can be introduced, so that the biomass produced by them can be utilized for production of various bioproducts.

Conversion Processes for First Generation Biofuels
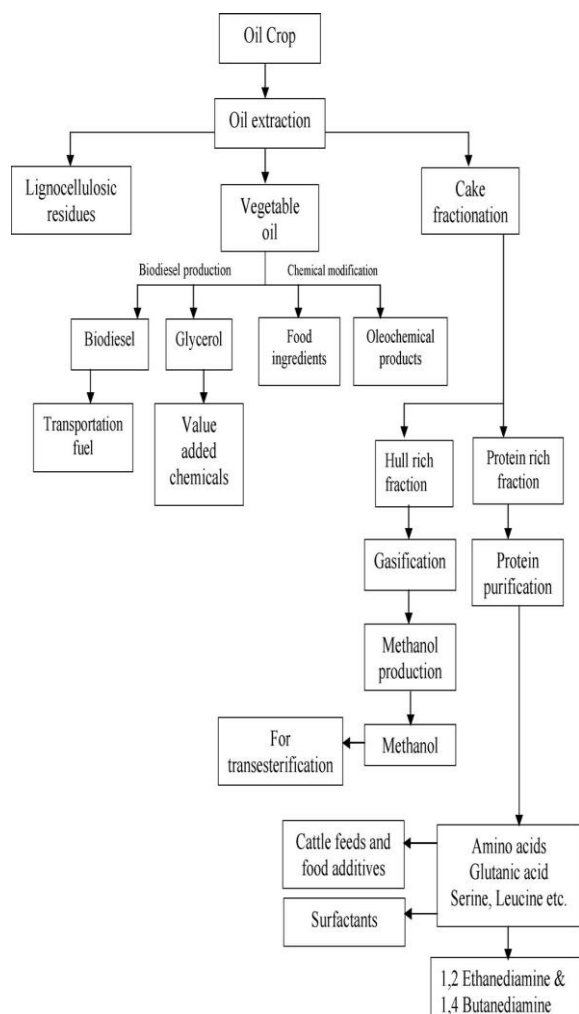### Transesterification

Figure 1 Whole crop biorefinery.

The vegetable oil based fatty acid methyl esters (FAME), popularly known as biodiesel, is gaining importance as an environment-friendly diesel fuel substitute or extender.

Biodiesel is an alternative diesel, made from renewable biological sources such as vegetable oils and animal fats by chemically reacting oil or fat with an alcohol, in the presence of a homogeneous and heterogeneous catalyst as given in figure 1. The product of the reaction is a mixture of methyl esters, which are known as biodiesel, and glycerol, which is a high value co-product [23, 24].

Homogeneous Catalysis

Transesterification is a reversible reaction and proceeds essentially by mixing the reactants in which the catalysts is a liquid acid or a liquid base. The process is known as transesterification.

Heterogeneous Catalysis

It is not possible to perform a basic transesterification process for high free fatty acid (FFA) content oil and decreases the conversion of oil to methyl ester due to saponification reaction. The use of solid catalyst is recommended for high free fatty acid containing oil. This is because the solid acid catalysts can simultaneously catalyze the transesterification of triglycerides and esterification of free fatty acid (FFA) present in oil to methyl esters. Solid acid catalysts have the strong potential to replace homogeneous catalysts, eliminating separation, corrosion and environmental problems [23].

The solid acid catalyzed biodiesel production by simultaneous esterification and transesterification of low quality oil containing high FFA was performed by Kulkarni et al. As given in figure 2 [23]. The esterification takes place between free fatty acids (RCOOH) and methanol (CH_3OH) whereas transesterification takes place between triglyceride (RCOOR') (taken as representative of triglycerides in this case) and methanol adsorbed on acidic site (L+) of catalyst surface. The interaction of the carbonyl oxygen of free fatty acid or monoglyceride with acidic site of the catalyst forms carbocation. The nucleophilic attack of alcohol to the carbocation produces a tetrahedral intermediate. During esterification the tetrahedral intermediate eliminates water molecule to form one mole of ester ($RCOOCH_3$).

The transesterification mechanism can be extended to tri- and di-glyceride. It is well known that transesterification is a stepwise reaction. In the reaction sequence the triglyceride is converted stepwise to di- and monoglyceride and finally glycerol. The tetrahedral intermediate formed during reaction eliminates di-, monoglyceride and glycerol when tri-, diand monoglyceride come in contact with the acidic sites, respectively, to give one mole of ester ($RCOOCH_3$) in each step. In cases, esterification and transesterification produce methyl ester, the same final product. The catalyst is regenerated after the simultaneous esterification and transesterification reactions. Use of excess alcohol favours forward reaction and thus maximize the ester yield [23].

Ethanol Conversion Processes.
A wide variety of carbohydrates containing raw materials have been used for production of ethanol by fermentation process.

These raw materials are classified under three major categories:
a) Sugar containing crops: Sugar cane, wheat, beet root, fruits, palm juice, etc.
b) Starch containing crops: Grain such as wheat, barley, rice, sweet sorghum, corn, etc. and root plants like potato, cassava.
c) Cellulosic biomass: Wood and wood waste, cedar, pine, wood, etc. agricultural residues, fibres.
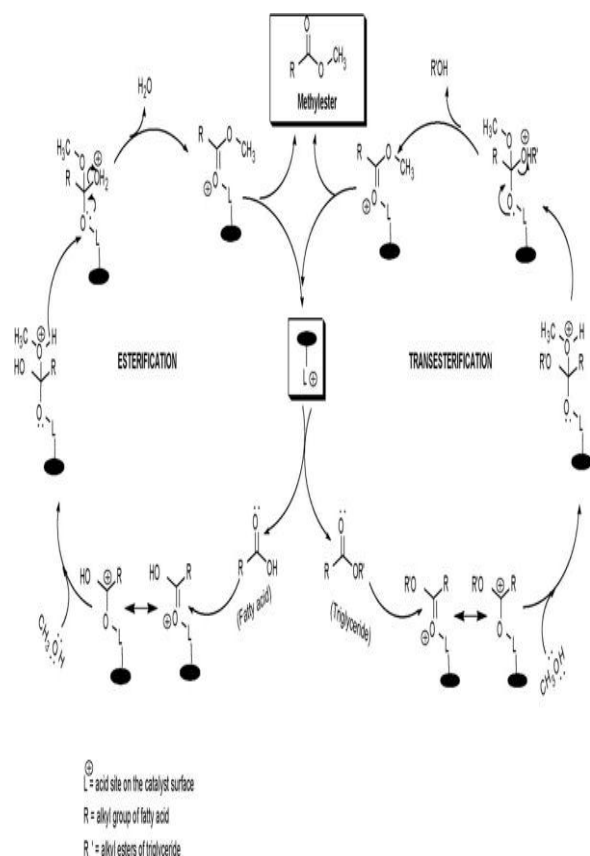
Figure 2 Solid acid catalyzed simultaneous esterification and transesterification.

The alcohol produced from food crops like corn, wheat, barley, sweet sorghum is called grain alcohol, where as ethanol produced from lingo-cellulosic biomass such as agro residue (i.e. rice straw, wheat straw) grasses (switch grass) is known as biomass ethanol or bioethanol. Both these alcohols are produced through biochemical process [25].

Chemical structure of starch consists of long chain polymer of glucose. The macromolecular starch cannot be directly fermented to ethanol by conventional fermentation technology. The macromolecular structure first broke down in to simpler and smaller glucose. In this process, starch feedstocks are grounded and mixed with water to produce a mash typically contained 15–20% starch. The mash is then cooked at or above its boiling point and treated subsequently with two enzyme preparation. The first enzyme hydrolyzes starch molecules to short chains to glucose. The first enzyme is amylase, amylase liberates ''maltodextrin'' oligosaccharides by liquefaction process. The dextrin and oligosaccharides are further hydrolyzed by enzyme such as pullulanase and glucoamylase in a process known as saccharification. Saccharification converts all dextrans to glucose, maltose and isomatose. The mash is then cooled to 30°C and yeast is added for fermentation [26]. Ethanol production is usually obtained via enzymatic hydrolysis of starch containing crops like corn wheat. Corn ethanol production facilities can be classified into two groups i.e. wet & dry mill processes [25]. Dry mills are usually smaller in size (capacity) and are built primarily to manufacture ethanol only.

According to Shapouri et al. [27] modern wet milling plants are able to produce 1 gal ethanol consuming 35150 Btu of thermal energy and 2134 KWh of electricity. If molecular sieves are used the thermal energy input drops to 32150 Btu/gal. The starch grain is prepared for ethanol fermentation by either dry grinding or wet milling as shown in figure 3(a) and 3(b) respectively. Wet mill ethanol process produced variety of valuable coproducts such as nutraceuticals, pharmaceuticals, organic acids and solvent. Dry grinding mill process is specially designed for production of ethanol and animal feed.

Fermentation Process

The term fermentation can generally be defined as the metabolic process in which an organic substrate goes under chemical changes due to activities of enzymes secreted by micro-organisms. There are two basic types of fermentation (a) aerobic and (b) anaerobic depending upon oxygen needed in the process or not. There are thousands of micro-organisms in nature capable of providing fermentative changes. Some of these are capable of producing ethanol from sugar and starch. The microorganisms employed for ethanol production are classified into three categories viz. yeast (saccharomyces species), bacteria (zymomonas species), and mold (mycelium). These micro-organisms found in nature and are very selective in their fermentation characteristics, some of this ferment specific to hexoses or pentose, or mixtures of both. Efforts are being made by various researchers to produce ideal micro-organism, which will be able to produce ethanol from any carbohydrate.

Starch is polymer of glucose. Starch cannot be directly fermented to ethanol by conventional fermentation technology. In the process of fermentation, starch broken down glucose molecules once treated with yeast like saccharomyces cerevial, saccharomyces uvarum, schizosaccaharomyces pombe, and kluyveromyces species.

Under anaerobic conditions yeasts metabolize glucose to ethanol. However; some of the glucose is used by the yeast for production of cell mass and for metabolic products other than ethanol, thus reducing the conversion efficiency from its theoretical maximum. In practice, between 40 and 48% of glucose is actually converted to ethanol with 46% fermentation efficiency, i.e. 1000 kg of fermentable sugar would produce about 583 lit of pure ethanol (sp gravity at 20°C = 0.789) [26].

Anaerobic Digestion of Biomass

Anaerobic digestion of solid waste is a process very similar to that used in biogas production (Figure 4). Anaerobic bacteria in the absence of oxygen are used to break down the organic matter of biomass, and during the conversion a mixture of methane and carbon dioxide gases are produced. The typical ratio of gas mixture is 60–70% methane and 30% carbon dioxide. The gas has a heating value 650–750 Btu/ft3. Due to increase cost of energy, the anaerobic digestion of biomass is an attractive alternative for production of fuel and biofertilizer for organic cultivation. Anaerobic digestions in landfills are potential source of methane production from solid waste.

substitute for natural gas. The contaminants are toxic vinyl chloride and hydrogen sulphide [26]. The conventional use of land fill gas to energy include electricity generation using internal combustion engine, turbine, micro turbine, direct use in boiler, dryer, kiln, green house and cogeneration.

The current research of land fill gas focuses on the generation of liquid fuels instead of the gaseous fuel from anaerobic digestion due to the high cost associated for methane purification and collection [26]. Production of methanol as liquid has several advantages. First low sulphur, low ash fuels can be made for commercial use. Second, liquid fuel is much easier to handle, store and transport than gaseous products. By utilizing waste lignocellulosic biomass through anaerobic digestion process will generate liquid fuel and biofertilizer for Agricultural production. The biorefinery concept of anaerobic digestion is shown below.

Figure 4 Anaerobic digestions.

Whole-Crop Biorefinery

A whole-crop biorefinery processes and consumes the whole crop to obtain useful products. Raw materials such as oil seed can be used as feedstock in the unit operations of a whole crop biorefinery as depicted in Fig. 4. In that context, example of jatropha oil seed crop has been discussed. Jatropha seed kernel contains 35–40% oil and 1–1.5 tonnes of oil can be produced per ha [28]. The process of converting biomass into energy is initiated by separation of biomass into different components that are then treated separately. The oil obtained acts as the starting material for biodiesel production or can undergo chemical modification to produce oleochemical products, whereas the de-oil cake fraction after purification can be used as the basic raw materials for the synthesis of valuable chemicals or for gasification. The lignocellulosic biomass produced during the refinery operations can act as the starting material to the lignocellulosic biorefinery for the production of syngas, where syngas can be used as the basic material for the synthesis of fuels and methanol using the Fischer– Tropsh process.

Oleochemicals

Oleochemicals refer to chemicals derived from natural oils and fats of both plant and animal origins. Basically,
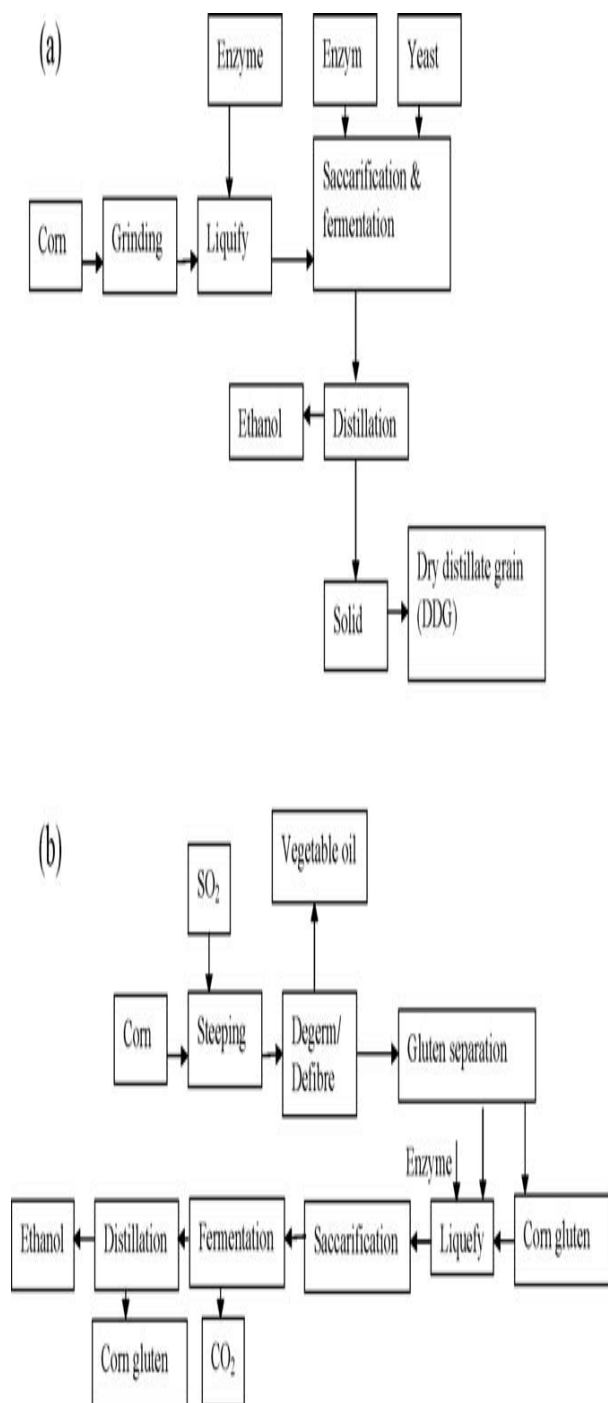
Figure 3 (a) Dry mill process and (b) Wet mill process.

Anaerobic digestion of biodegradable portion of the municipal solid waste (mostly biomass and biological waste) produces methane and carbon dioxide in roughly equal amount. These two principal components together with atmospheric nitrogen, oxygen and traces of organic compounds are known as landfill gas (LFG). According to Environmental Protection Agency (EPA), each pound of biodegradable organic waste can produce 10–12 standard cubic feet of gas. Landfill gas is similar to low quality natural gas, in that it requires the removal of the volatile organic contaminants and CO_2 to realize substantial commercial value. The removal of toxic and other contaminants from LFG require efficient separation technology to use it as a
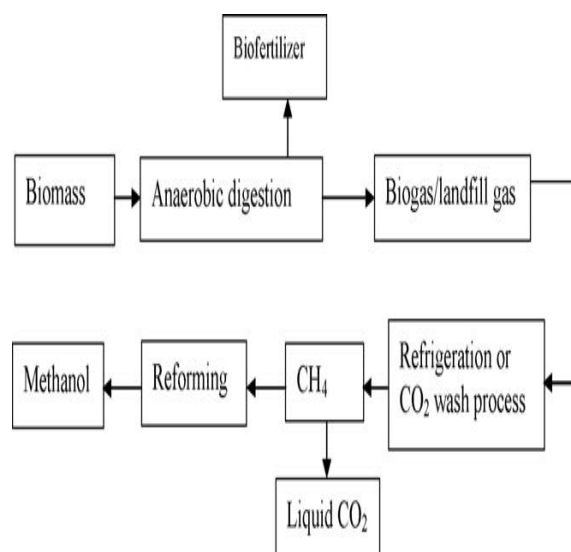
oleochemicals refer to the fatty acids and glycerol derived from the splitting of the triglyceride structures of oils and fats. However, they also include those derivatives derived from the subsequent modification of the carboxylic acid group of the fatty acids by chemical or biological means, and other compounds obtained from further reactions of these derivatives (Figure 5 (b)). Oleochemicals are often categorised into basic oleochemicals such as fatty acids, fatty methyl esters, fatty alcohols, fatty amines and glycerol. In fact, until the 1980s, almost 95% of natural oils and oils were used in foods and only a small percentage was used in non-food applications such as soap manufacturing and drying oils. It was only after the 1980s that oleochemicals found wide uses in both food and non-food, or technical applications which previously are the domains of ''synthetic chemicals'' derived from petroleum or better known as petrochemicals. At this moment, oleochemicals are used in the manufacture of such products as foods and specialty fats, soaps and detergents, cosmetics and personal care products, lubricants and greases, drying oil, surface coatings and polymers, and biofuels (Figure 5 (a)). In theory, oleochemicals can replace petrochemicals in all their applications [29]. Why oleochemicals? The reasons are simple First, oleochemicals are derived from renewable resources, as compared to petrochemicals which are obtained from exhaustible or non-renewable petroleum, Secondly, products derived from oleochemicals are more readily biodegradable and hence do not pose a threat to the environment, Thirdly, products derived from petroleum sources use more energy and cause higher emissions of such pollutants as NOx, SO2, CO and hydrocarbons.

De-Oil Cake

Biomass used for production of biodiesel would generate million tonnes of residual protein (De-oilcake). The use of protein for non-food applications is currently more limited compared to the utilization fatty acids derivatives. The edible protein can be utilized for production of essential amino acids for animal feeds and human consumption. Some of the nonedible oil seeds cake like jatropha, neem, karanja, etc. would use to produced biopesticides and amino acids for non-food applications. Sanders et al. [30] have reported the application of protein based raw materials for production of 1, 2 ethanediamine and 1, 4-butanediamine from amino acids. The production of amino acids from de-oil cake would add value to biofuel crops produce in large scale. 1, 2-Ethanediamine is produced starting with ethylene by various routes. 1, 2-Ethanediamine and 1, 4 butanediamine can be synthesized from amino acids such as serine and arginine respectively (Figure 6). Decarboxylation of serine will form ethanolamine, which is converted into diamine by addition of ammonia. Arginine can be hydrolysed to ornithine and urea. Ornithine will form 1, 4- butanediamine after carboxylation. Protein based surfactants are the most valuable mild surfactants. Since the structure and properties of the amino acids in the surfactants are similar to the tissue of the skin amino acids, this cause strong affinity and soft feeling on skin. Acyl derivatives from glutamic acid and serine are very effective in comparison with conventional surfactants. The production of protein based surfactant involves hydrolysis of protein with sulphuric acid followed by acylation with RCOCl (R55 C12–C18) to form acyl amino acid sodium salts which are converted into acylesters of amino acids by esterification with fatty alcohol [30].
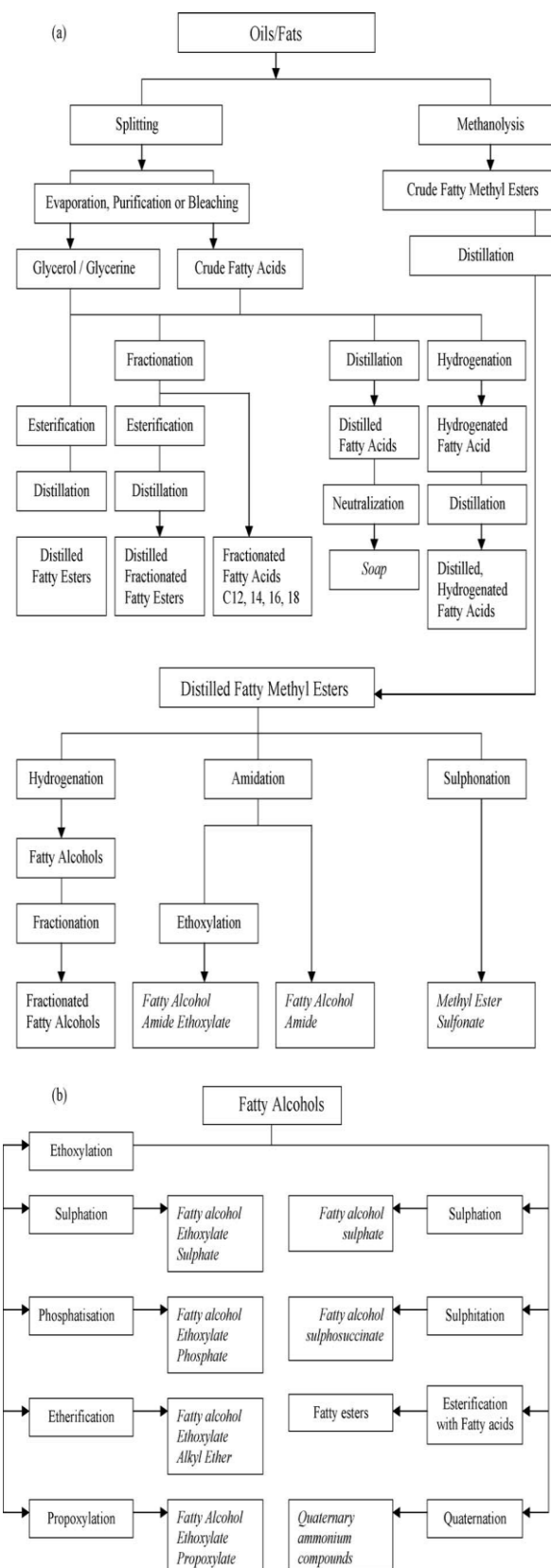

Figure 5 (a) Basic oleochemicals and downstream oleochemicals and derivatives and (b) Basic oleochemicals and downstream oleochemicals and derivatives production flow.
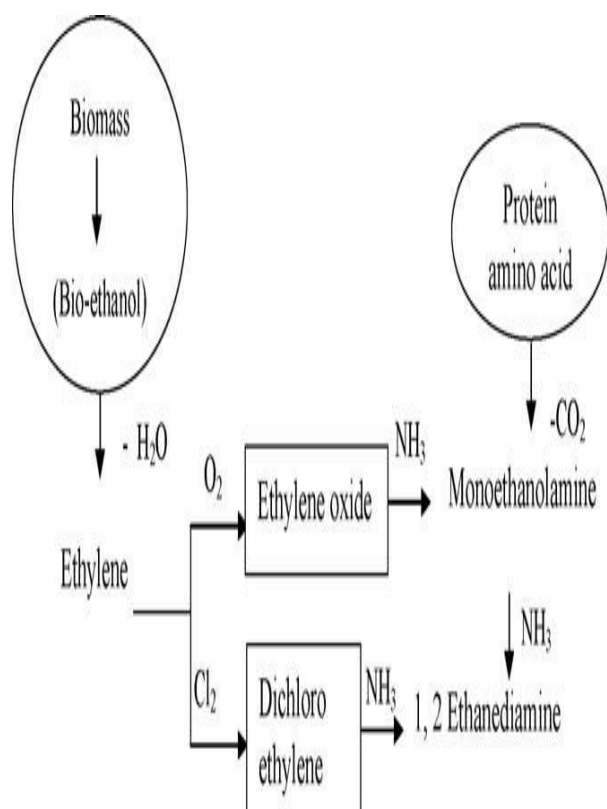
Figure 6 Production of 1, 2-ethanediamine using various routes.

SECOND GENERATION BIOFUELS

Second generation biofuels are produced from biomass in a more sustainable fashion, which is truly carbon neutral or even carbon negative in terms of its impact on CO_2 concentrations. In the context of biofuel production, the term 'plant biomass' refers largely to lignocellulosic material as this makes up the majority of the cheap and abundant non-food materials available from plants [11,31]. At present, the production of such fuels is not cost-effective because there are a number of technical barriers that need to be overcome before their potential can be realized.

Plant biomass represents one of the most abundant and underutilized biological resources on the planet, and is seen as a promising source of material for fuels and raw materials. As it is most basic, plant biomass can simply be burnt in order to produce heat and electricity. However, there is great potential in the use of plant biomass to produce liquid biofuels. Plant biomass is comprised mostly of plant cell walls, of which typically 75% is composed of polysaccharides [32]. These polysaccharides represent a valuable pool of potential sugars, and even in traditional food crops such as wheat (Triticum aestivum) there is as much sugar tied up in the stems as there is in the starch of the grains. To date, the potential of many crop residues, such as straw and wood shavings, to provide sugar feedstocks for biofuel production has not been realized. However, biofuel production from agricultural by-products could only satisfy a proportion of the increasing demand for liquid fuels. This has generated great interest in making use of dedicated biomass crops as feedstock for biofuel production [22].

Lignocellulosic materials are a collection of feedstocks for advanced biofuels and can be obtained either through hydrolysis and fermentation (i.e. bioethanol) or through gasification (i.e. Fischer–Tropsch bio-diesel, bio-DME and bio-SNG). Typical resources for these fuels are short rotation forestry crops (poplar, willow and eucalyptus), perennial grasses (miscanthus, switch grass and reed canary grass) and residues from the wood industry, forestry and from agriculture. Advanced biofuels, also referred to as 2nd generation biofuels, are carbon-based fuels that are produced by innovative processes mainly using lignocellulosic materials for which commercial utilization is still under development.

Bioethanol (advanced) is a substitute of gasoline. It is a full substitute for gasoline in so-called flexi-fuel vehicles. With hydrolysis, sugars are extracted from lignocellulosic feedstock, after which the sugars are fermented into ethanol. Fischer–Tropsch diesel (FT-diesel) or BTL (Biomass-to-Liquids) is a full substitute of diesel. Lignocellulosic biomass is gasified to produce syngas which is in turn transformed into liquid hydrocarbons, mostly diesel and kerosene. Bio-SNG (Synthetic Natural Gas) is a fuel that can be used in gasoline vehicles with slight adaptations.
Lignocellulosic biomass is gasified to produce syngas which is in turn transformed into methane. Bio-DME (Dimethyl Ether) is a fuel that can be used in diesel vehicles with slight adaptations. Lignocellulosic biomass is gasified to produce syngas which is in turn transformed into DME [33].

Conversion Processes for Second Generation Biofuels

There are two main routes available for producing liquid biofuels from biomass; one involves thermochemical processing and the other biochemical processing. Thermochemical processing defines the conversion of biomass into a range of products, by thermal decay and chemical reformation, and essentially involves heating biomass in the presence of different concentrations of oxygen. The clear advantage of thermochemical processing is that it can essentially convert all the organic components of the biomass compared with biochemical processing which focuses mostly on the polysaccharides [11]. This section onwards paper mainly focuses on the conversion processes for lignocellulosic biomass and utilization of combination of technologies for production of other value added chemicals and example of some biorefineries based on different feedstocks have been discussed aiming at the integrated utilization of biomass (Figure 7)

Physical Conversion
Mechanical Extraction

Crude vegetable oils are recovered from the oil seeds by applying a mechanical pressure using screw press (expeller). Screw press can be applied in two ways: prepressing and full pressing. In pre-pressing, only part of the oil is recovered and the partially de-oiled meal (cake with 18–20% oil) is further treated by solvent extraction. Combined pre-pressing and solvent extraction is commonly applied for oilseeds with high oil content (30–40%). Full pressing requires 95,000 kPa to squeeze out as much oil as possible, preferably up to 3–5% residual fat for animal materials. Full-pressing can also be carried out in a prepress and a final press [7].
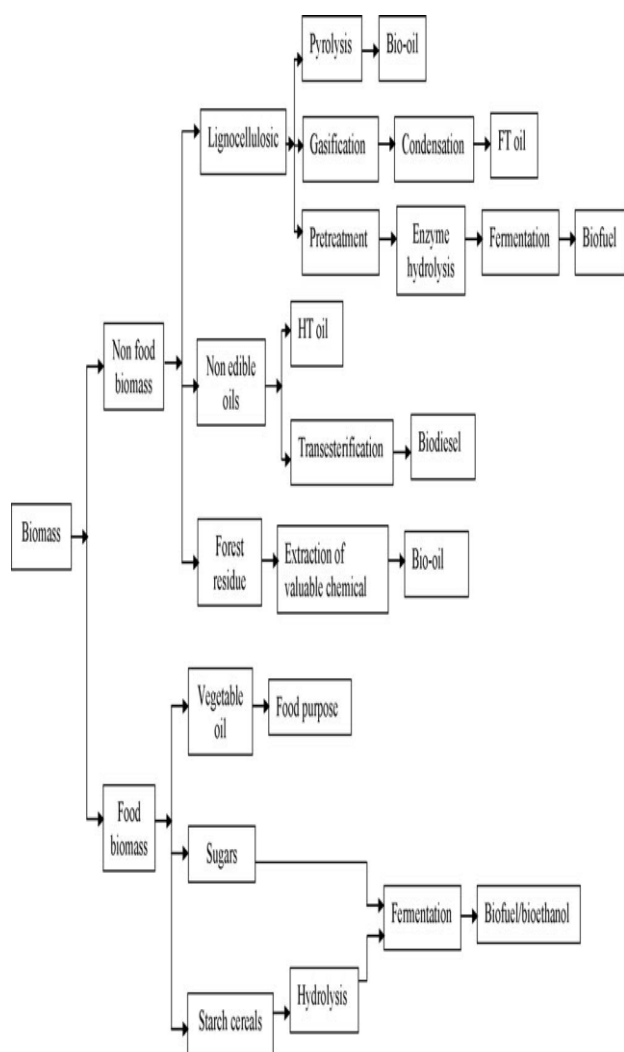
Figure 7 Second generation biofuel production from biomass

Briquetting of Biomass

Agricultural, forestry residues and other waste biomass materials are often difficult to use as biofuels because of their uneven bulky and troublesome characteristics. This draw back can be overcome by means of densification of the residual into compact regular shapes. During densification biomass enclosed in compression chambers presses. There are two major methods of densification, i.e. pressing and maceration. Some time these two processes are combined, in pressing there is a close correlation of an increase in density with an increase in applied pressure in the early stage of compression, but the rate of increase in density fall rapidly as the density of pressed material approaches the density of water. There is no such close correlation of density change and degree of maceration, which may be chopping, grinding, and pulverizing. A coarse chopping of some materials may be as effective as ultrafine grinding. For example tree branches undergo extensive volume reduction when chipped, but fine grinding would provide little, if any, additional reduction in volume [6, 7].

Distillation

Distillation is the most important method for extracting essential oil and relies on the evaporation of the more volatile constituents of a blend to separate them from the non-volatile parts. Plants are crushed to encourage them to release their oils. The plants are steam distilled, and the essential oils vaporize and rise up with the steam. The vapours are captured, and are allowed to condense back into liquids. A more high tech chemical process is molecular distillation. It is used to produce fragrances that cannot be distilled by conventional methods [7].

Thermo-Chemical Conversion

Biomass can be converted to energy by mainly two processes. They are either thermo-chemical or biological. The thermochemical conversion process includes direct combustion, gasification, liquefaction, and pyrolysis. When biomass is heated under oxygen deficient conditions, it generates synthesis gas, or syngas, which consists primarily of hydrogen and carbon monoxide. This syngas can be directly burned or further processed for other gaseous or liquid products. In this sense, thermal or chemical conversion of biomass is very similar to that of coal [26].

Direct Combustion.

Combustion is the chemical reaction between a fuel and oxygen which usually takes place in air and is more commonly known as burning. The products are carbon dioxide and water with the release of heat. When the direct combustion of biomass is conducted in a well vented area, biomass burning used for domestic stoves and boilers can be a sound substitute for combustion of conventional fissile fuel. Sulphur emissions (0.05–0.2 wt %) are much lower and the formation of particulate can be controlled at the source [26].

Gasification

Generally gasification is not a new technology however its use for the conversion of biomass into a viable fuel has only been investigated for past thirty years. Syngas can be produced from biomass by two routes namely catalytic and noncatalytic. Noncatalytic process requires a very high temperature of operation, as high as 1300°C, whereas catalytic process can be operated at substantially lower temperature. With more advances in the catalysis, the temperature requirement is expected to go downward further from the current value of about 900°C [26]. The gasification step involves reacting biomass with air, oxygen, or steam to produce a gaseous mixture of CO, CO_2, H_2, CH_4, and N_2 either known as producer gas or synthesis or syngas, depending on the relative proportions of the component gases [18].

Producer gas is primarily useful as a fuel for stationary power generation, whereas syngas may be, and is presently, used to make a range of fuels and chemical intermediates. For transportation fuels, the main syngas derived routes to fuels are hydrogen by water-gas-shift reaction (WGS) [34], hydrocarbons by Fischer–Tropsch (F-T) synthesis or methanol synthesis followed by further reaction to produce hydrocarbon or oxygenated liquid fuels [33]. The WGS reaction uses CO, H_2O to give H_2 and CO_2. It can be used to upgrade producer gas to syngas by enriching the H2 content or to produce H2 as an end product in its own right. F-T synthesis has been used since 1930s to produce hydrocarbon fuels from syngas. The production of methanol from syngas has been practiced since the 1920s [18].

Liquefaction

The liquefaction of biomass has been investigated in the presence of solution of alkalis, glycerine, propanol, butanol or direct liquefaction [35]. Liquefaction usually produces water insoluble oils of high viscosity and usually requires solvents, reducing gases such as CO or H_2 and/or catalysts to be present in addition to biomass [18]. In the field of thermochemical conversion of biomass, lignocellulosic materials can be converted directly to a liquid similar to heavy fuel oils by reacting them with synthesis gas in the presence of suitable catalyst [36]. Aqueous liquefaction of lignocellulosics involves desegregation of the wood ultra structure, followed by partial depolymerisation of the constitutive compounds. In the alkali liquefaction, deoxygenating occurs through decarboxylation from ester formed by hydroxyl group and formate ion derived from carbonate.

Alkali salts such as sodium carbonate and potassium carbonate, can act as catalyst for hydrolysis of macromolecules such as cellulose and hemicellulose into smaller fragments. The heavy oil obtained from the liquefaction process is a viscous tarry lump, which sometimes caused troubles in handling. For this reason, some organic solvents (e.g. propanol, butanol, acetone, methyl ethyl ketone, ethyl acetate) need to be added to the reaction system. All these solvents, except ethyl acetate, may be reproduced from wood during liquefaction. This suggests that the solvent can be recovered for reuse. The oil yield is reported to be higher with the catalytic aqueous liquefaction than with the non-catalytic aqueous liquefaction. The average oil yield is around 31% in the non catalytic process and 63% in the catalytic process [35].

In the liquefaction process, the amount of solid residue increased in proportion to the lignin content. Lignin is a macromolecule, which consists of alkylphenols and has a complex three dimensional structure. It is generally accepted that free phenoxy radicals are formed by thermal decomposition of lignin above 525 K and that the radicals have a random tendency to form solid residue through condensation and polymerization. Bio-oil obtained from air dried wood by high pressure liquefaction (HPL) result in a complex mixture of volatile organic acids, alcohols, aldehydes, ethers, esters, ketones, and non volatile components. These oils could be upgraded catalytically to yield an organic distillate product which is rich in hydrocarbons and useful chemicals. Compared to bio-oil obtained from the fast pyrolysis method, their yield from HPL process is much lower and highly viscous [35].

Pyrolysis

The pyrolysis is thermal degradation of biomass by heat in the absence of oxygen, which results in the production of charcoal (solid), bio-oil (liquid), and fuel gaseous products. The pyrolysis of biomass has been studied with the final objectives of recovering a biofuel with medium-low calorific power [35]. Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: (a) Conventional pyrolysis, (b) Fast pyrolysis, and (c) Flash pyrolysis.

Conventional Pyrolysis

Conventional pyrolysis occurs under a slow heating rate (0.1–1 K/s) and residence time is 45– 550 s and massive pieces of wood. In the first stage of biomass decomposition which occurs in between 550 and 950 K is called pre-pyrolysis. During this stage, some internal rearrangement such as water elimination, bond breakage, appearance of free radicals, formation of carbonyl, carboxyl and hydroperoxide group take place [37]. The second stage of solid decomposition corresponds to the main pyrolysis process. It proceeds with a high rate and leads to the formation of pyrolysis products. During the third stage, the char decomposes at a very slow rate and it forms carbon rich solid residues.

Fast Pyrolysis

It occurs in the high temperature range of 850–1250 K with fast heating rate (10–200 K/s), short solid residence time (0.5–10 s) and fine particle (<1 mm). The fast pyrolysis is recommended for production of liquid and/or gaseous products. In fast pyrolysis process biomass decomposes to generate vapours, aerosol, and some charcoal like char. After cooling and condensation of vapours and aerosol a dark brown mobile liquid is formed that has heating value that is half that of conventional fuel oil. Fast pyrolysis produced 60–75% of bio-oil, 15–25% solid char and 10–20% non condensed gases depending upon feedstocks [37].

Flash Pyrolysis

It differs strongly from that of conventional pyrolysis, which is performed slowly with massive pieces of wood. It occurs in the temperature range of 1050–1300 K, fast heating rate (>1000 K/s), short residence time (<0.5 s) and very fine particle (<0.2 mm) (Figure 8). Bio-oil production from biomass pyrolysis is typically carried out via flash pyrolysis [35] the produced oil can be mixed with the char to produce bioslurry. Bioslurry can be more easily fed to the gasifier (gasifier condition: 26 bars; 927–1227 K) for efficient conversion to syngas. The conversion of biomass to crude oil can have an efficiency of up to 70% for flash pyrolysis process. The so called bio-crude can be used in engines and turbines. Its use as feedstocks for refineries is also being considered [35, 38].

Hydrotreating of Vegetable oils/Green Diesel

Vegetable oils are renewable feedstock currently being used for production of biofuels from sustainable biomass resources. The existing technology for producing diesel fuel from plant oils such as rapeseed, soybean, canola and palm oil are largely centred on transesterification of oils with methanol to produce fatty acid methyl esters (FAME) or biodiesel. The future widespread use of biofuels depends on developing new process technologies to produce high quality transportation fuels from biologically derived feedstocks. These new biofuels need to be compatible with the existing fuel and transportation infrastructure to be economically feasible.

Researchers around the world are in pursuit of different processing routes to convert vegetable oils into a high quality diesel fuel or diesel blend stock that would fully compatible with petroleum derived diesel fuel. The isoparaffin-rich diesel known as 'green diesel' is produced from renewable

feedstock containing triglycerides and fatty acids by process of catalytic saturation, hydrodeoxygenation, decarboxylation and hydroisomerization. This technology can be widely used for any type of oil feedstock to produce an isoparaffin-rich diesel substitute. This product, referred to as green diesel, is an aromatic and sulphur free diesel fuel having a very high cetane blending value.

The cold flow properties of the fuel can be adjusted in the process to meet climate-specific cloud point specifications in either the neat or blended fuel [39]. Green diesel has a higher cetane value and good cold flow properties. It is also has excellent storage stability and is completely compatible for blending with the standard mix of petroleum derived diesel fuels. In contrast to fatty acid methyl esters, green diesel properties do not depend on feed origin and process configuration and the fully deoxygenated biofuel is readily blended with diesel fuel.

Bio-Oil
Bio-oil/pyrolysis oil is produced by fast pyrolysis process. In this process, organic class of compounds, such as cellulose, hemicellulose, and lignin, etc. are thermally decomposed at moderate temperature (400°C–600.8°C) in absence of oxygen to produce liquid product viz. bio-oil (60–70%), char (13–25%), and gas such as CO, H_2, light hydrocarbons (13–25%). The yield and chemical composition of bio-oil depends upon feed stocks and process condition: particle size of biomass (2–5 mm), residence time (0.1– 2 s), and reactor type. In general, reactor types which are presently used are; fluidized bed reactor, circulating fluid bed, fast fluidized bed, etc. The bio-oil is a dark brown viscous, corrosive and acidic with distinctive smoky odour used as fuel for boiler, gas turbine, diesel engines, furnaces and stationary engines.

Bio-oil has a complex chemical composition contained chemical products of lignocelluloses biomass like aliphatic alcohols/aldehydes, furanoids, pyranoids, benzenoids, fatty acids and high molecular mass hydrocarbons, etc. these constituents are mixed with water (25 -45%), which is formed in pyrolysis process to form an emulsion with organic constituents. Therefore a wide range of ''Green Chemicals'' can be extracted from bio-oil by solvent extraction. The Supercritical fluid extraction such as supercritical CO_2 can selectively extract the value added chemicals from bio-oil. These chemical compounds can be utilized for natural resin, food flavours, wood preservatives, slow release fertilizer, pharmaceuticals, etc. [40–45].

Ft Oil or Green Motor Fuel from Biomass
Franz Fisher and Hans Tropsch first studied conversion of syngas (CO + H_2) in to large number of useful organic compounds in 1923. The syngas produced by gasification of biomass can be converted into large number of organic compounds. The process of converting CO and H_2 mixture into liquid fuels or hydrocarbons over transition metal catalyst is known as Fisher-Tropsch oil (FT oil) or Green motor fuel. The FT synthesis processes have flexibility in feed stocks (coal, biomass, natural gas) and the fuel produced by FTS process contains low sulphur. The major drawback of FTS process is the polymerization in the process which yields very high molecular mass waxes which need to be hydrocracked to produce green diesel. Some of the recent publication indicates that the use of FT process technology

for biomass conversion to synthetic hydrocarbon may be promising and carbon neutral alternative to conventional fuels. The flow chart for FT process is shown below as Figure 9. Biomass gasification can provide the opportunity to convert biosyngas into green fuels such as H_2 and FT oil.
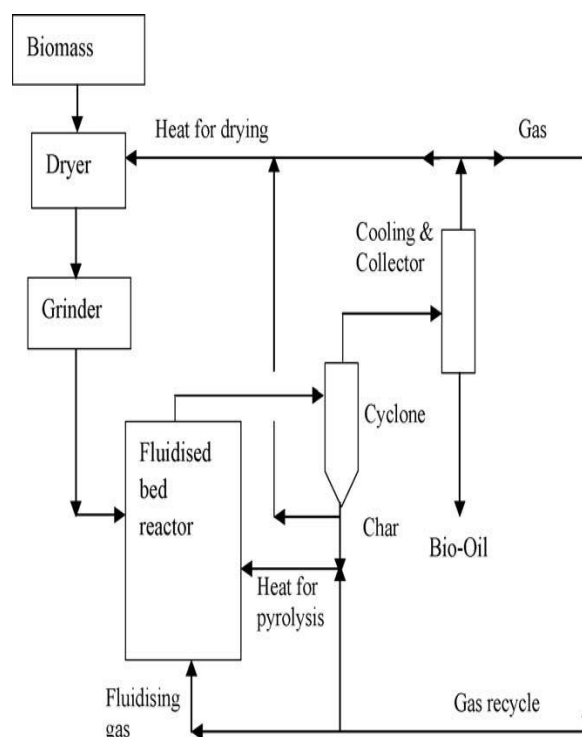

Figure 8 Fluidized bed fast pyrolysis process.

The biomass gasification produces biosyngas, which contains degraded products of biomass such as carbohydrate (cellulose, hemicellulose) and lignin. The gas mixtures consists of carbon monoxide (28– 36%), carbon dioxide (22–32%), hydrogen (21–30%), methane (8– 11%), benzene/toluene/xylene (0.84–0.96), ethane (0.16–0.22), tar (0.15–0.24) [33]. All the reactions are exothermic and the product is a mixture of different hydrocarbons in that paraffin and olefins are main parts. In FTS one mole of CO reacts with two mole of H_2 in the presence of catalyst to form a hydrocarbon chain. The products from FTS are mainly aliphatic straight chain hydrocarbons. Besides the straight chain hydrocarbons, branched hydrocarbons and primary alcohol are also formed in minor quantities.

The product distribution obtained from FTS include light hydrocarbon methane (CH_4), ethylene (C_2H_4) and ethane (C_2H_5), LPG (C3–C4), propane (C3), butane (C4), gasoline (C5–C12), diesel fuel (C13–C22) and wax (C23–C33). Some raw biomass contained traces of contaminants such as NH_3, H_2S, HCl, dust and alkali in ash. The distribution of products depends upon the catalyst and process parameters such as temperature, pressure, and residence time [45].

Bioethanol from Lignocellulosic Biomass
Biological conversion technologies are based on microbial and enzymatic process for producing sugars from biomass

such as lignocellulosic, starch, cellulosic. The sugars later can be converted into alcohol and other solvents of interest to fuel and chemicals. For example, yeast based fermentation has shown good yield for ethanol from sugar or starch crops. Solid waste has been used to produce methane through anaerobic digestion in fabricated digesters or landfill. The production of ethanol from corn, sugarcane by biochemical means has already been commercially established. It is essential to hydrolyze lignocellulose for biological conversion.
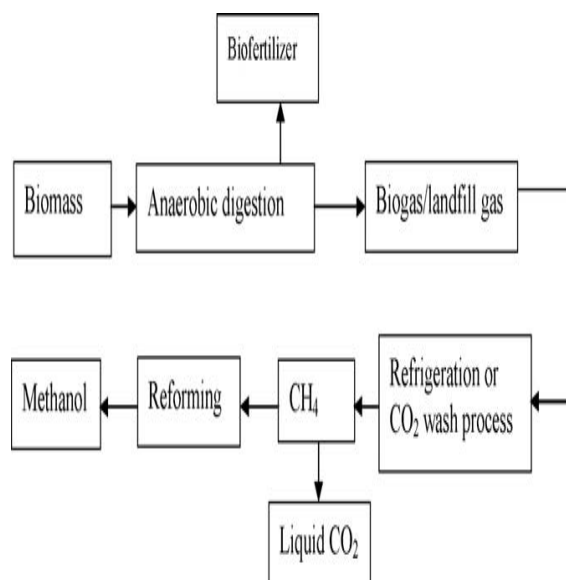

Figure 9 Biomass based FT synthesis process.

Enzymatic hydrolysis of lignocellulosic biomass required some research and developmental work to increase the yield of alcohol. The conversion of biomass feed stocks to liquid fuels such as ethanol requires a number of basic unit operations including pre-treatment, enzyme production, hydrolysis, fermentation and ethanol recovery. Biomass to ethanol research emphases on reduced costs which requires improved cellulose and hemicellulose conversion to sugar, combined xylose and glucose fermentation, lower pre-treatment energy requirements, conversion of lignin to value added products, and efficient separation process for alcohol [25,26]. Agricultural residues, forest residue, post harvest processing of Industrial food crops generate enormous amounts of carbohydrate containing lignocellulosic waste [46]. This lignocellulosic biomass consists of three main structural units: cellulose, hemicelluloses and lignin. Cellulose is crystalline glucose polymer and hemicelluloses are amorphous polymers of xylose, arabinose, and lignin a large poly aromatic compounds. The conversion of complex lignocellulosic biomass to alcohol is more difficult as compared to starch based feedstocks. The conversion of lignocellulosic biomass to alcohol requires three step process i.e. pre-treatment of biomass, acid or enzymatic hydrolysis and fermentation/distillation. The pre-treatment processes separate xylose and lignin from the crystalline cellulose [47].

The steam explosion process is an efficient pre-processing method for converting lignocellulosic biomass (Figure 10). In this process biomass sample is placed in a pressure vessel

(i.e. digester) and vaporized using saturated steam for a short time (20 s to 20 min) at a temperature 473–543 K and high pressure 14–16 bar. The pressure in digester is then dropped quickly by opening the steam and the material is exposed to normal atmospheric pressure to cause explosion which disintegrate lignocellulosic biomass. Different types of devices are available for steam explosion. Steam explosion causes the hemicellulose and lignin from the wood to be decomposed and converted into low molecular weight fractions which can be easily extracted. Therefore most of the water soluble fraction of hemicellulose can be removed by water extraction. At the same time, a part of the low molecular weight fraction of lignin is also extracted. The xylose can be fermented to ethanol and the lignin can be further processed to produce other fuels. The crystalline cellulose remains solid after the pre-treatment and later break down to glucose by enzymatic hydrolysis process. The glucose is further fermented to alcohol and the hemicellulose fraction is converted to xylose. The conversion of xylose to ethanol is a difficult process, therefore, pre-treatment is necessary to reduce the crystallinity of cellulose to lessen the average polymerization of the cellulose and hemicellulose–lignin sheath that surround the cellulose and to increase available surface area for the enzyme to attack [25].

Ethanol can be blended with gasoline to produce an oxygenated fuel with lower hydrocarbon and green house gas emissions, certain aldehydes are increased, which could cause health issues. Automobiles can be operated on ethanol/gasoline blends from 5% to 25% without any alterations in engine equipments or setting [25]. The major engine operation issue with alcohol blended fuels is fuel quality, volatility, octane number, cold start, hot operation, and fuel consumption.
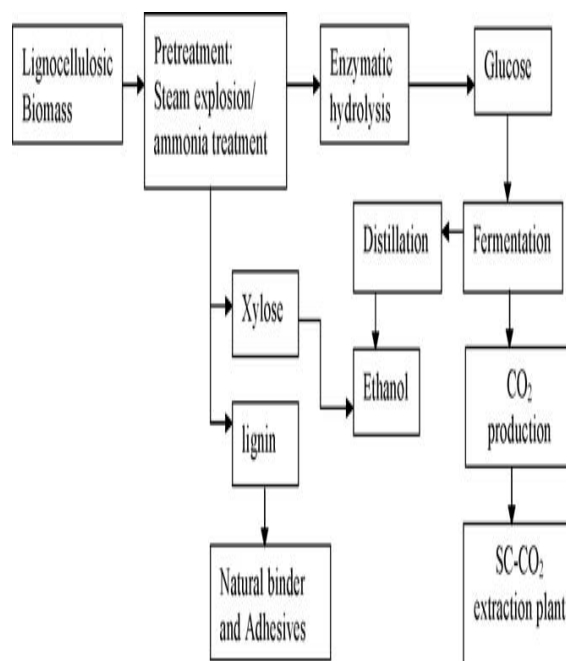

Figure 10 Conversion of lignocellulosic biomass to ethanol.

Chemical Conversion
Chemical Hydrolysis
The important specific factors in chemical hydrolysis are surface to volume ratio, acid concentration, temperature, and

time. The surface to volume ratio is especially important, in that it also determines the magnitude of the yield of glucose. Hence smaller the particle size the better the hydrolysis in terms of the extent and rate of reaction. With respect to the liquid to solid ratio, the higher the ratio the faster the reaction [48].

Solvent Extraction

Solvent extraction involves different unit operations: extraction of the oil from the oil seeds using hexane as a solvent; evaporation of the solvent; distillation of the oil–hexane mixture (called miscella); and toasting of the de-oiled meal. In special cases, other solvents can be used: halogenated solvents (mostly dichloromethane), acetone, ethanol or isopropanol. Supercritical extraction can also be performed using CO_2 [7]. Extraction refers to a process in which the desired substance is selectively removed from the raw materials by allowing the desired substance to dissolve into the solvent, and subsequently recovering the substance from the solvent. To remove the particular substance from biomass, extraction and separation are both essential. Typically biomass (wood, wheat straw, aromatic grasses, etc.) contains high volume of macromolecular compounds (polysaccharide, cellulose hemicellulose, and lignin) called primary metabolite. The other low volume and high value biochemical molecules like terpenoids, waxes, resins, sterols, and alkaloids are known as secondary metabolites or extractive biomass. In the biorefinery process these chemicals are initially extracted from biomass by using solvent extraction or supercritical fluid extraction.

Recently Dewarte et al. [49], Clark et al. [16] reported integrated straw based biorefinery and isolated high value chemicals like waxes, polycosanol, and sterol by using supercritical carbon dioxide. Supercritical fluid extraction can be used for extraction of aromatic woods (cedar wood, sadal wood, pine wood) to isolate extractives. The extracted lignocellulosic biomass is further used for hydrolysis and fermentation for production of biofuels. The other solvent like, ethanol, acetone, methanol, water can be used to isolate desired extractive from biomass [7].

Supercritical Water Conversion of Biomass

A supercritical fluid is defined as a substance that is at temperature and pressure conditions which are above its vapour liquid critical point (for water it is 644 K and 22 MPa; for CO_2 it is 304 K and 7.4 MPa). At supercritical conditions a fluid is neither liquid nor gas as it cannot be made to boil by decreasing the pressure at constant temperature, and it would not condense by cooling at constant pressure [50]. Supercritical fluid processing of biomass to chemicals represents an alternative path to acid hydrolysis, enzymatic hydrolysis of cellulose to sugars. With acid hydrolysis acid recovery is a costly and polluting issue. Enzymatic saccarification needs pre-treatment of lignocellulosic biomass. Supercritical water can quickly convert cellulose to sugar and convert biomass into a mixture of oils, organic acids, alcohol and methane. In supercritical (i.e. 300– 644 K; pressure 200–250 bar) and near critical state (523–573 K) acid (H+) and base components (OH-) of water are separate and dissolve in the biomass. The dissolved supercritical water breaks the bonds of cellulose and hemicellulose rapidly to produce small sugar molecules, glucose, xylose and oligosaccharide [51, 52]. These properties make supercritical water a very promising reaction

medium without using any catalyst for the conversion of biomass to value added products.

Supercritical water gasification technology has been demonstrated for conversion of cellulose into glucose in the range of 10–20 s and above 45 s pyrolysis start (Figure 11). As temperature increases to 873 K supercritical water becomes strong oxidant and results in complete disintegration of the substrate structure by transfer of oxygen from water to the carbon atoms of the substrate. The hydrogen atom of water is set free and form hydrogen. Supercritical water also breaks the cellulosic bonds and also formed gaseous products.
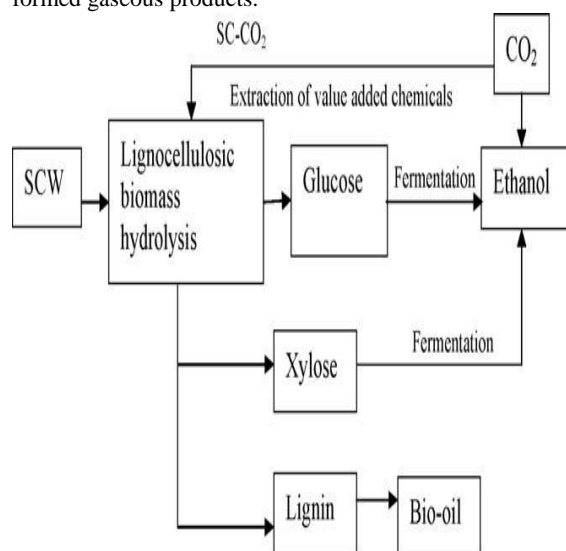

Figure 11 Supercritical water conversion of biomass.

TYPES OF BIOREFINERY

Green Biorefinery

A green biorefinery is a multiproduct system which handles its refinery cuts, products, and fractions in accordance with the physiology of the corresponding plant material as described by Kamm and Kamm [21], Fernando et al. [12]. A green biorefinery uses natural wet feedstocks derived from untreated products, such as grass, green plants, or green crops as inputs, which are produced in large quantities in green plants. The first step of the refinery is to treat the green biomass substances in their natural form using wet-fractionation to produce a fibre-rich press cake and a nutrient-rich green juice. The press cake contains cellulose, starch, valuable dyes and pigments, crude drugs, and other organics, whereas the green juice includes proteins, free amino acids, organic acids, dyes, enzymes, hormones, other organic substances, and minerals. The pressed cake can be also used for the production of green feed pellets, as a raw material for the production of chemicals, such as levulinic acid, and for conversions to syngas and synthetic fuels.

Forest and Lignocellulosic Based Biorefinery

Lignocellulosic materials contain two types of polysaccharides, cellulose and hemicellulose, bound together by a third component, lignin. LCB consists of three basic chemical fractions, (i) hemicellulose, sugar molecule of mainly pentoses, (ii) cellulose, a glucose polymer, (iii) lignin, polymer of phenols [54]. In LCB mainly uses hard fibrous plant materials generated by lumber or municipal waste. In

the initial step plant material are cleaned and broken down into three fractions (hemicellulose, cellulose, and lignin) using chemical digestion or enzymatic hydrolysis. Hemicellulose and cellulose can be produced by alkaline (caustic soda) and sulphite (acidic, bisulphite, alkaline, etc.).

The sugar polymers (cellulose and hemicellulose) are converted to their component sugars through hydrolysis. In case of hemicellulose, it consists of short, highly branched chains of sugars. It contains five carbon sugars usually D-xylose and arabinose, six carbon sugars and uronic acid. The hydrolysis of cellulose to glucose can be carried out either by enzymatic processing or chemical processing which produces useful products such as ethanol, acetic acid, acetone, butanol, and other fermentation products. Although the hemicelluloses and cellulose fractions have numerous uses it is not yet the case for lignin. However, there are still some unsatisfactory parts within the LCB, such as utilization of lignin as fuel, adhesive or binder. It is unsatisfactory because the lignin scaffold contains considerable amounts of mono-aromatic hydrocarbons which, if isolated in an economical way, could add a significant value to the primary processes. Because the primary technologies would generate primary chemicals from which industry could make a wide range of fuels, chemicals, materials, and power. Therefore five stages have been suggested: sugar stage, thermochemical or syngas stage, biogas stage, carbon rich chains, and plant products.

Aquatic or Algae-Based Biorefinery

Algae are photosynthetic microorganisms that convert sunlight, water and carbon dioxide to lipids or triaceylglycerol. The lipids may include neutral lipids, polar lipids, wax esters, sterols and hydrocarbons as well phenyl derivatives such as tocopherols, cartenoids, terpenes, quinones, and phenylated pyrole derivatives such as chlorophylls. Algae have high growth rates and tolerance to varying environmental conditions. They can survive and reproduce in low quality high saline water [6]. This feature has allowed algae to be used in wastewater treatment plants for sludge treatment (Gray). In addition, since they have high CO_2 tapping and fixation ability, so the algae can be utilized to reduce carbon dioxide emission from power plants and other industries with high carbon dioxide emission [55]. Algae or cynobacteria can be used in bioreactors to reduce CO_2 emission from power plants and use the algae biomass for oil extraction and biodiesel production. There are over 40,000 species of algae have been identified and many more yet to be identified, algae are classified in multiple major groupings. Algae synthesize fatty acids principally for esterification of glycerol based membrane lipids which constitutes about 5–20% of their dry cell weight (DCW). Fatty acids include medium chain (C10–C14), long chain (C16–C18) and very long chain (C19-C20) species of fatty acid derivatives. Hydrocarbons and other types of neutral lipid are found in algae at a quantity less than 5%. Bortyococcus braunii has been shown to produce large quantities of (up to 80% DCW) of very long chain (C23–C20) hydrocarbons, similar to those found in petroleum and thus explored as feedstocks for biofuel and biomaterials. Oil content of some algae species exceeds 80% of the dry weight of algae [56]. Agricultural oil crops such as soybean, rapeseed and oil palm are widely used to produce biodiesel. For example, palm oil, one of the most productive oil crops

yields only 6000 Litre of oil per hectare, whereas microalgae oil yield per hectare is around 58,700 l/ha [57].

The potential advantages of algae as feedstocks (biofuels and biomaterials) for biorefinery are as follows:
1) Algae synthesize and accumulate large quantities of neutral lipids/oil (20–50% DCW),
2) High growth rates (1–3 doublings/day),
3) Thrives in saline/brackish water/costal sea water,
4) Algae tolerate marginal lands (e.g. desert, arid and semi arid land) that are not suitable for conventional agriculture,
5) Utilize growth nutrients such as nitrogen and phosphorus from variety of wastewater sources (e.g. agricultural runoff, industrial and municipal waste water),
6) Sequester CO_2 from flue gases emitted from fossil fuel fired power plants and other sources there by reducing emissions of a major greenhouse gas,
7) Produced value added co-products or by products (e.g. biopolymers, proteins, polysaccharides, pigments, animal feed, fertilizer and H_2).
8) Algae can be grown in suitable culture vessel (photo-bioreactor) throughout the year with an annual biomass production.

Integrated Biorefinery

The biorefinery types that have been discussed previously are based on one conversion technology to produce various chemicals. A biorefinery is a capital-intensive project, and when it is based on just one conversion technology, as is the case for the previously described biorefineries, it increases the cost of outputs (or products) generated from such biorefineries. Hence, several conversion technologies (thermochemical, biochemical, etc.) can be combined together to reduce the overall cost, as well as to have more flexibility in product generation and to provide its own power. Three different platforms, namely: thermochemical, sugar, and nonplatform or existing technologies are integrated. An integrated biorefinery produces various products, which include electricity produced from thermochemical and bioproducts from the combination of sugar and other existing conversion technology platforms. An emerging concept in the biorefinery arena is conversion of bio-oil, the product from biomass pyrolysis, which could be routed via a conventional petrochemical refinery to generate various chemicals. The advantage of this route is that all necessary infrastructures for the separation and purification of products generated are already in place. This concept makes perfect sense since most petroleum refineries are well equipped to handle variable feedstock with the assumption that no two batches of crude oil are the same.

Bio-oil chemical properties vary with the feedstock but woody biomass typically produces a mixture of 30% water, 30% phenolics, 20% aldehydes and ketones, 15% alcohols, and 10% miscellaneous compounds [58]. A process known as hydrodeoxygenation (HDO) could be applied to replace oxygen by hydrogenation of the raw bio-oils. After several HDO treatment steps the bio-oil could be transformed into a liquid hydrocarbon with properties similar to those of petroleum crude oil. The deoxygenated bio-oils can potentially be refined in existing petroleum refineries, with only minor adjustments to the current petroleum industry

refinery infrastructure that is set up for hydrodesulphurization (HDS) process [59].

COSTS, PRICES AND ECONOMIC IMPACTS OF BIOFUELS

In previous economic studies of biodiesel production, the main economic factors such as capital cost, plant capacity, process technology, raw material cost and chemical costs were determined [43]. The major economic factor to consider for input costs of biodiesel production is the feedstock, which is about 75–80% of the total operating cost. Other important costs are labour, methanol and catalyst, which must be added to the feedstock [63]. Using an estimated process cost, exclusive of feedstock cost, of US$0.158/l for biodiesel production, and estimating a feedstock cost of US$0.539/l for refined soy oil, an overall cost of US$0.70/l for the production of soy-based biodiesel was estimated [64]. Palm oil is the main option that is traded internationally, and with potential for import in the short term [65]. The oil in the vegetable seeds is converted into biodiesel through oil extraction, oil refining, and transesterification.

The cost of biodiesel can be lowered by increasing feedstock yields, developing novel technologies, and increasing economic return on glycerol production by finding other uses for this by-product, which, at the moment, due to oversupply is sold for little or no value. Alternatively, the use of co solvents, such as tetrahydrofuran, can make the alcohol–oil–ester–glycerol system into a single phase, thereby reducing the processing costs [10]. However, these improvements still would not make biodiesel economically competitive at the current stage.

Biofuels production costs can vary widely by feedstock, conversion process, scale of production and region. On an energy basis, ethanol is currently more expensive to produce than gasoline in all regions considered. Only ethanol produced in Brazil comes close to competing with gasoline. Ethanol produced from corn in the US is considerably more expensive than from sugar cane in Brazil, and ethanol from grain and sugar beet in Europe is even more expensive. These differences reflect many factors, such as scale, process efficiency, feedstock costs, capital and labour costs, co-product accounting, and the nature of the estimates.

The cost of large-scale production of bio-based products is currently high in developed countries. For example, the production cost of biofuels may be three times higher than that of petroleum fuels, without, however, considering the non-market benefits. Conversely, in developing countries, the costs of producing biofuels are much lower than in the OECD countries and very near to the world market price of petroleum fuel [38]. The cost of feedstock is a major economic factor in the viability of biodiesel production. Nevertheless, the price of waste cooking oil is 2.5– 3.5 times cheaper than virgin vegetable oils, thus can significantly reduce the total manufacturing cost of biodiesel. Biodiesel obtained from waste cooking vegetable oils has been considered a promising option. Waste cooking oil is available with relatively cheap price for biodiesel production in comparison with fresh vegetable oil costs. Economic advantages of a biofuel industry would include value added to the feedstock, an increased number of rural manufacturing jobs, an increased income taxes, investments in plant and

equipment, reduced greenhouse gas emissions, reduced a country's reliance on crude oil imports and supported agriculture by providing a new labour and market opportunities for domestic crops. In the recent years, the importance of non-food crops increased significantly.

The opportunity to grow non-food crops under the compulsory set-aside scheme is an option to increase the biofuel production. Renewable liquid fuels such as ethanol, biodiesel, green diesel, and green gasoline are important because they replace petroleum fuels. The renewable liquid fuels are generally considered as offering many priorities, including sustainability, reduction of greenhouse gas emissions, regional development, social structure and agriculture, and security of supply [5].

The socioeconomic impacts on the local economy arising from providing power through renewable resources instead of conventional generation technologies are very important. These impacts include direct and indirect differences in the jobs, income, and gross output. There are significant socioeconomic impacts associated with the investment in a new power plant, including increases in employment, output, and income in the local and regional economy. Increases in these categories occur as labour is directly employed in the construction and operation of a power plant, as local goods and services are purchased and utilized. The potential for reduced costs of renewable liquid fuels and conservation of scarce fuel resources results in significant reductions in fuel usage. In addition to these economic benefits, development of renewable resources will have environmental, health, safety and other benefits.

Agriculture ethanol is at present more expensive than synthesis- ethanol from ethylene. The simultaneous production of biomethanol (from sugar juice) in parallel to the production of ethanol appears economically attractive in locations where hydro- electricity is available at very low cost [66].

Currently there is no global market for ethanol. The crop types, agricultural practices, land and labour costs, plant sizes, processing technologies and government policies in different regions considerably vary ethanol production costs and prices by region. The cost of producing ethanol in a dry mill plant currently totals US$1.65/ gallon. Corn accounts for 66% of operating costs while energy (electricity and natural gas) to fuel boilers and dry DDG represents nearly 20% of operating costs [67].

Ethanol from sugar cane, produced mainly in developing countries with warm climates, is generally much cheaper to produce than ethanol from grain or sugar beet in International Energy Agency (IEA) countries. For this reason, in countries like Brazil and India, where sugar cane is produced in substantial volumes, sugar cane-based ethanol is becoming an increasingly cost-effective alternative to petroleum fuels. Ethanol derived from cellulosic feedstock using enzymatic hydrolysis requires much greater processing than from starch or sugar-based feedstock, but feedstock costs for grasses and trees are generally lower than for grain and sugar crops. If targeted reductions in conversion costs can be achieved, the total cost of producing cellulosic ethanol in OECD countries could fall below that of grain ethanol. Estimates show that ethanol in the EU becomes competitive when the oil price

reaches US$70 a barrel while in the United States it becomes competitive at US$50–60 a barrel. For Brazil the threshold is much lower – between US $25 and US $30 a barrel. Other efficient sugar producing countries such as Pakistan, Swaziland and Zimbabwe have production costs similar to Brazil's [68]. Anhydrous ethanol, blend able with gasoline, is still somewhat more expensive.

Prices in India have declined and are approaching the price of gasoline. In general United States conversion plants produce biofuels, particularly ethanol, at lower cost than plants in Europe. Production costs for ethanol are much lower in countries with a warm climate, with Brazil probably the lowest-cost producer in the world. Production costs in Brazil, using sugar cane as the feedstock, have recently been recorded at less than half the costs in Europe. Production of sugar cane ethanol in developing countries could provide a low-cost source for substantial displacement of oil worldwide over the next 20 years. For biofuels, the cost of crop feedstock is a major component of overall costs.

In particular, the cost of producing oil-seed-derived biodiesel is dominated by the cost of the oil and by competition from high-value uses like cooking. The largest ethanol cost component is the plant feedstock. Operating costs, such as feedstock cost, co-product credit, chemicals, labour, maintenance, insurance and taxes, represent about one third of total cost per litre, of which the energy needed to run the conversion facility is an important (and in some cases quite variable) component. Capital cost recovery represents about one-sixth of total cost per litre. It has been showed that plant size has a major effect on cost [69]. The plant size can reduce operating costs by 15–20%, saving another $0.02–$0.03 per litre. Thus, a large plant with production costs of $0.29 per litre may be saving $0.05–$0.06 per litre over a smaller plant [70]. Biodiesel from animal fat is currently the cheapest option ($0.4– $0.5/l) while traditional transesterification of vegetable oil is at present around $0.6–$0.8/l [71]. Rough projections of the cost of biodiesel from vegetable oil and waste grease are, respectively, $0.54–$0.62/l and $0.34–$0.42/l. With pre-tax diesel priced at $0.18/l in the United States and $0.20–$0.24/l in some European countries, biodiesel is thus currently not economically feasible, and more research and technological development will be needed [72].

BIOFUEL POLICY OF INDIA
Biofuel policy of India has announced an ambitious biofuel policy in 2009 to substitute 20% of petroleum fuels in transportation by bioethanol and biodiesel. Some of the critical aspects of the biofuel policy are as follows: the 20% target is only advisory or indicative and not yet mandatory, though a mandatory level of 10% for bioethanol exists but yet to been forced. It recognizes the need for adopting sustainable production criteria, however, no such criteria applicable to Indian conditions currently exists.

Only non-edible oil seeds are considered for biodiesel production, due to the shortage of edible oils in India. Export of biofuels to be banned till domestic needs are completely met. Further there is a ban on importing free fatty acid (FFA) oils for biofuel production and imported biofuels will be subjected to taxes, duties and levies. However, domestically produced biodiesel is exempt from all taxes and duties. The

focus of biofuel production will be on marginal or wastelands owned by the government, communities and forest departments. Use of irrigated, fertile land for biofuel production is discouraged, though it may be difficult to enforce such a condition. This encourages deployment of degraded lands and prevents competition with food production. Corporate sector has been permitted to undertake contract farming, involving the farmers. However, foreign direct investment (FDI) in plantations is not permitted. Biofuel production is targeted for not only meeting the transportation demand but also meeting the needs of decentralized power generation. This creates incentives for the local communities, especially if community lands are involved.

The biofuel policy addresses the price uncertainties to biofuel producers by announcing a minimum guaranteed support price for the feed stock produced. Thus, the Indian biofuel policy is progressive to the extent that it aims to promote sustainable production systems, focuses on deploying marginal or wastelands and discourages the use of fertile crop lands to avoid competition with food production, provides price incentives to biofuel producers, bans foreign companies in investing directly in plantation activities for biofuel production. India will have to quickly formulate sustainable biofuel production criteria and develop institutional arrangements to enforce many of the provisions of the biofuel policy.

In the below given figure we can have an idea about the Biofuel crops, feed-stocks and fuels present in India which is according to the Biofuel policies of India. (Figure 12)

CONCLUSION
Today, the world is facing three critical problems: (1) high fuel prices, (2) climatic changes and (3) air pollution. Currently there are several important problems to be resolved worldwide: (1) high need for energy, (2) high depletion of non-renewable energy recourses and (3) high local and global environmental pollution [75, 76]. Discussions on biofuels include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. The biggest difference between biofuels and petroleum feedstocks is oxygen content. Biofuels have oxygen levels from 10% to 45% while petroleum has essentially none making the chemical properties of biofuels very different from petroleum. Oxygenates are just pre used hydrocarbons having structure that provides a reasonable antiknock value [77]. Most traditional biofuels, such as ethanol from corn, wheat, or sugar beets, and biodiesel from oil seeds, are produced from classic agricultural food crops that require high-quality agricultural land for growth. Ethanol is a petrol additive/substitute. Production of ethanol from biomass is one way to reduce both the consumption of crude oil and environmental pollution.
Biodiesel is an environmentally friendly alternative liquid fuel that can be used in any diesel engine without modification. There has been renewed interest in the use of vegetable oils for making biodiesel due to its less polluting and renewable nature as against the conventional petroleum diesel fuel. Biofuels have become more attractive recently because of its environmental benefits. Ethanol addition to gasoline has increased the engine torque, power and fuel

consumption and reduced carbon monoxide (CO) and hydrocarbon (HC) emissions. In general, biodiesel increases NOx emissions when used as fuel in diesel engine. The emissions of biodiesel (B20 and B100) for same model compression–ignition (diesel) vehicles have increased from 1.86 to 2.23, respectively. The fact that NOx emissions increase with increasing biodiesel concentration could be a detriment in areas that are out of attainment for ozone. Oxygenated diesel fuel blends have a potential to reduce the emission of particulate matter (PM) and to be an alternative to diesel fuel. Biofuels production costs can vary widely by feedstock, conversion process, scale of production and region. The major economic factor to consider for input costs of biodiesel production is the feedstock, which is about 75–80% of the total operating cost.
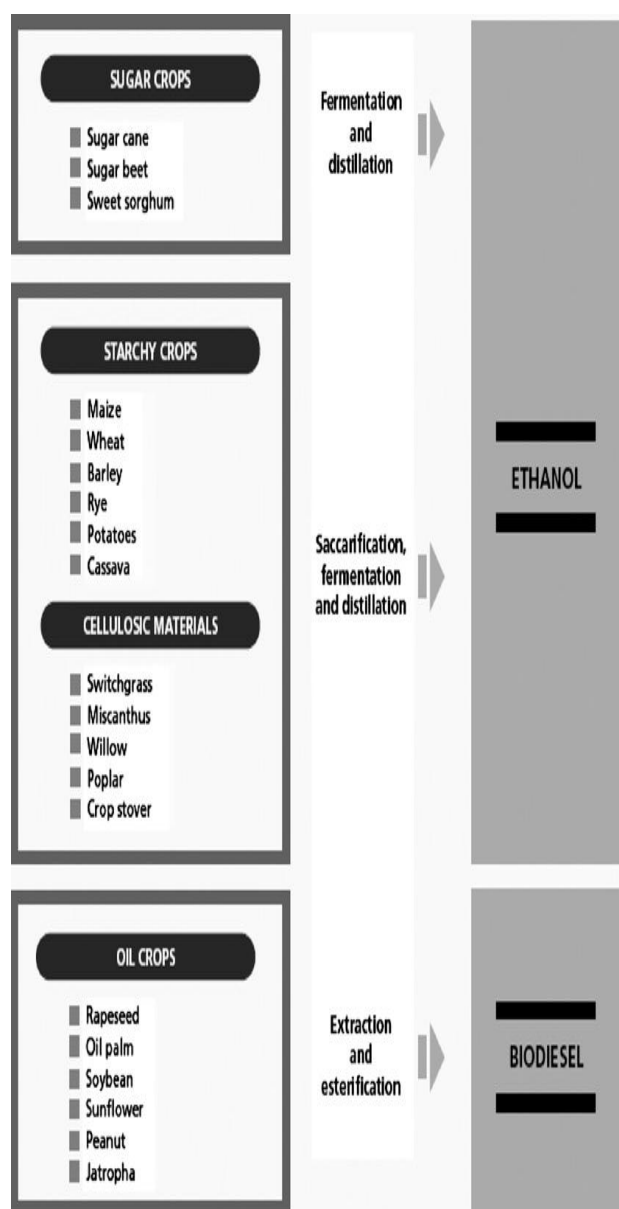
Other important costs are labour, methanol and catalyst, which must be added to the feedstock. In particular, the cost of producing oilseed- derived biodiesel is dominated by the cost of the oil and by competition from high-value uses like cooking. On an energy basis, ethanol is currently more expensive to produce than gasoline in all regions considered. The simultaneous production of biomethanol (from sugar juice) in parallel to the production of ethanol appears economically attractive in locations where hydroelectricity is available at very low cost. Production costs for ethanol are much lower in countries with a warm climate.

''Sustainable biofuel production systems could play a highly positive role in mitigating climate change, enhancing environmental quality and strengthening global economy but it will take sound, science based policy and additional research'' .

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Figure 12 Biofuel crops, feed-stocks and fuels in India. Source: FAO (2008)

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